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A TECHNIQUE TO MEASURE THE SPECIFIC HEAT OF REACTIVE MATERIALS BY HEAT FLOW CALORIMETRY

PAUL F. BUNYAN

Royal Armament Research and Development Establishment, Powdermill Lane, Waltham Abbey, Essex EN9 1AX (Gt. Britain)

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ABSTRACT

A novel technique to measure specific heat by monitoring the heat flow from a sample following a small, but rapid, drop in the operating temperature of a heat flow calorimeter is described. The technique is shown to be particularly useful for materials which generate heat by exothermic decomposition or by reaction with container materials. The specific heats of a variety of materials measured in this manner are reported and it is concluded that the method is capable of providing information for use in self-heating hazard prediction.

INTRODUCTION

In order to predict the self-heating behaviour of thermally unstable materials it is desirable to know the specific heat capacity of the material in the temperature region where self-heating commences.

A number of very sensitive methods for the determination of specific heat capacity have been reported. Picker et al. [1] have described a flow system suitable for liquid samples and Suurkuusk and Wadsö [2] have measured the heat capacity of both solids and liquids using a precise drop calorimeter. When a less accurate figure for specific heat is sufficient, various differential scanning calorimetry (DSC) methods are routinely employed. Demensky and Teplov [3] have recently reported the thermal capacities of a number of minerals using both periodic and continuous heating methods with a SETERAM DSC III and have found that the periodic method is more accurate than continuous heating.

The chemically reactive nature of thermally unstable materials, which can be expected to present self-heating problems, means that these methods are inappropriate in many cases, since the heat generated either by exothermic decomposition or by incompatibility between the sample and the walls of the calorimeter container, will influence the thermal capacity measurement.

A situation occurred recently in this laboratory, when the specific heats of a number of liquid propellants were required to interpret the result of accelerating rate calorimetry experiments. A novel use of the bioactivity monitor, where samples were contained in compatible glass tubes inside stainless steel ampoules while the temperature of the whole system was dropped by 1° C, provided acceptable values in these cases. Heat flow from samples was recorded by computer and used to deduce their thermal capacities.

The technique appeared generally applicable to problems of this type and an account of its development and assessment is described here.

GENERAL PRINCIPLES

The bioactivity monitor (BAM) is designed for the continuous measurement of low levels of heat generation from samples held at a constant temperature. Its instrumentation and detection principle are described in ref. 4.

If the set temperature is dropped by a small amount, a temperature gradient will develop between the ampoule containing the sample and the large heat sink of the detection block. The ampoule and contents will then cool until they reach the temperature of the rest of the system.

During this time, the heat flow from the ampoule will be proportional to the output voltage from the thermoelectric detector surrounding the sample ampoule and the difference between the integrated signal from the reference and sample sides of the detection system will be proportional to the difference in thermal capacity of the two ampoules and their contents.

In this manner, by measuring the total heat capacity difference between a reference of known thermal capacity and an unknown, under similar conditions (i.e. through the same temperature drop), the thermal capacity of the unknown sample can be deduced.

As the thermal capacities of the two ampoules cannot be perfectly matched, especially if a glass liner is used to prevent the sample from contaminating the stainless steel ampoule, a blank must be subtracted from both the known and unknown signals, before a comparison is made. Blank, uncorrected signal and corrected signal curves for a sample of alumina are illustrated in Fig. 1.

Practical difficulties involved in obtaining complete integral up to the point where the whole system reaches thermal equilibrium

After a change in instrument operating temperature, the ampoule temperature approaches that of the surrounding heat sink asymptotically with time. This will lead to long experiment duration if the entire decay region is to be recorded and could lead to inaccuracy in the final area measurement for the following reasons.

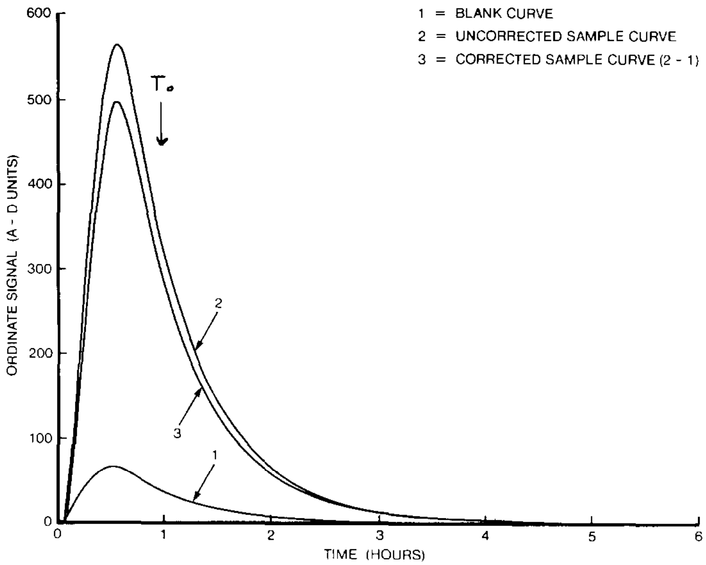

Fig. 1. Blank, uncorrected signal and corrected signal curves for an alumina sample.

(a) As the duration of the experiment increases, the imbalance signal of interest will decay, but the noise level will remain constant. Thus the signal-to-noise ratio will become increasingly unfavourable for long experiments.

(b) It is difficult to maintain a constant baseline for long periods of time, especially when sample and reference ampoules have very different thermal capacities. Diurnal variation of ambient temperature will tend to cause cycling of the baseline.

(c) At elevated temperatures it is necessary to top up the water circulating system to replace evaporation losses every few hours. This tends to cause a large "kick" in the baseline, especially if the sample and reference ampoules are of different thermal capacities.

These features are shown on typical temperature-drop induced imbalance peaks in Figs. 2 and 3.

It is therefore desirable to be able to obtain the entire peak area from data recorded solely in the first couple of hours of the experiment, when noise will be a small fraction of the signal and the baseline can be held constant.

The integral of the decay region of the curve may be obtained by analytical solution if heat loss from the ampoule can be shown to obey Newton's law of cooling, as follows.

Integration of the decay region of the imbalance peak from data recorded over its early stages

Newton's law of cooling states that the rate of cooling of a body under given conditions is directly proportional to the temperature difference

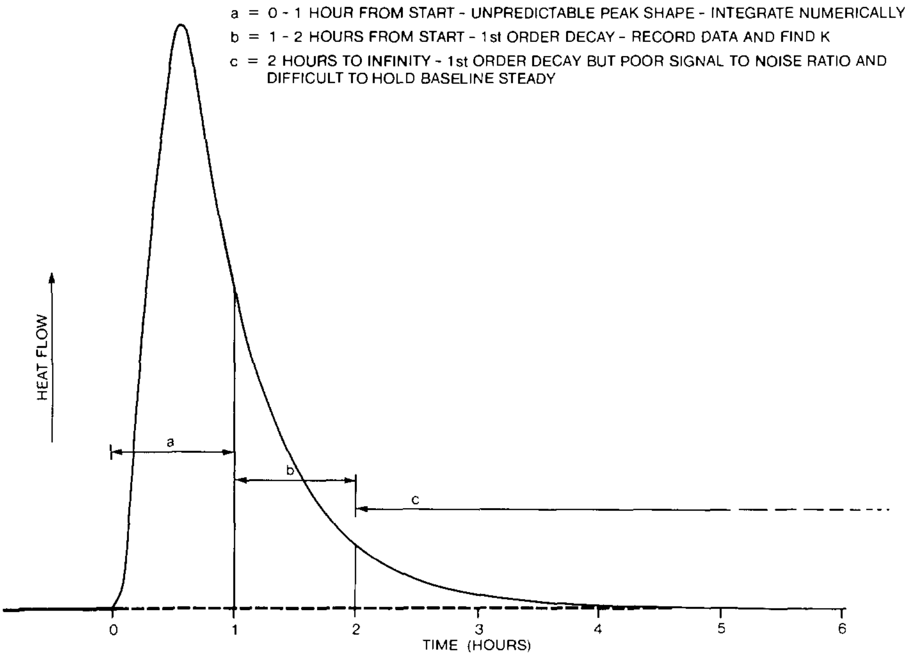

Fig. 2. Typical imbalance peak—to show various regions of curve.

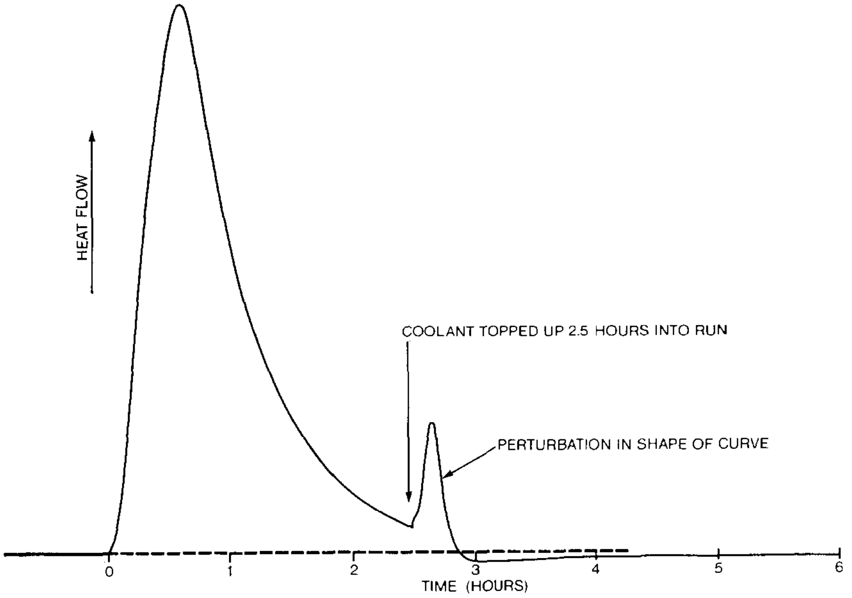

Fig. 3. Typical imbalance peak—to show effect of adding cold water to the circulating system reservoir.

between the body and its surroundings. This law is approximate, but is generally accepted as being true for small temperature differences.

Thus, once the rest of the system has reached thermal equilibrium (at time t_0 in Fig. 1), the ordinate signal will follow a first-order decay with time, provided Newton's law is obeyed

$$\ln(D/D_0) = -kt \qquad (1)$$

where D_0 = initial ordinate signal (in arbitrary analog to digital converter units), D = ordinate signal (in arbitrary analog to digital converter units) at time t, t = time (s) and k = decay constant (s^{-1}).

This can be rearranged to give a straight line relationship

$$\ln D = \ln D_0 - kt$$

If the cooling law is valid, a plot of log deflection versus time should give a straight line of negative gradient equal to the proportionality constant k.

Once the rate at the point when the decay region starts (in arbitrary analog to digital converter units) and the cooling rate constant (s^{-1}) are known, the area to infinity can be found analytically

From eqn. (1)

$$\ln(D/D_0) = -kt$$

taking antilog of each side

$$D/D_0 = e^{-kt}$$

making D the subject of the equation

$$D = D_0 \, e^{-kt}$$

then

$$\int_{t=0}^{t=\infty} D \, dt = \int_{t=0}^{t=\infty} D_0 \, e^{-kt} \, dt$$

$$= \left[D_0 - 1/k \; e^{-kt}\right]_0^{\infty}$$

$$= \left[D_0 - 1/k \; e^{-\infty}\right] - \left[D_0 - 1/k \; e^{0}\right] = D_0/k$$

Thus the area beneath the entire curve can be found by adding the integral of the first part of the peak (found by numeric integration since the curve will follow a complicated and unpredictable shape as the temperature of the entire system is varying) to the integral of the decay region.

When the corrected areas for samples of known and unknown specific heat are available, the specific heat of the unknown sample is given by

$$S_u = \frac{W_k \times A_u \times S_k}{W_u \times A_k}$$

where S_u = specific heat of unknown sample (J g^{-1} K^{-1}), W_k = weight of known sample (g), A_u = area of peak given by unknown sample, S_k = specific heat of known sample (J g^{-1} K^{-1}), W_u = weight of unknown sample (g) and A_k = area of peak given by known sample.

EXPERIMENTAL AND RESULTS

Equipment and materials

An LKB 2277 microcalorimeter (bioactivity monitor) was used for this work. Samples were contained in 9 × 46 mm glass tubes within standard 5 cm^3 stainless steel ampoules. An alumina specific heat calibration sample was obtained from MSE Scientific Instruments (α-Al_2O_3 Mettler part no. 29801). Trebly distilled mercury was obtained from Alexander Pickering and Co Ltd.

Heat generation data from the BAM were logged, stored and processed using a Hewlett Packard HP86b microcomputer system. Details of the hardware and software employed are described elsewhere [5].

Experimentation

All measurements were made for a temperature drop from 77 to 76 °C using the experimental procedure described in steps (1)–(14) below. The specific heat of the alumina calibration sample was taken to be 0.8717 J g^{-1} K^{-1} as reported by Ginnings and Furukawa [6].

(1) Empty glass sample tubes were placed within the sample and reference 5 cm^3 stainless steel ampoules. (2) Each ampoule was lowered into the equilibration region of a BAM cylinder for 30 min. (3) Each ampoule was then lowered into the detection region of the cylinder and the temperatures of the ampoule, cylinder and surrounding water bath were allowed to equilibrate. (4) The operating temperature of the BAM was dropped by 1 °C by adjusting the decade resistors on the temperature regulation unit. The subsequent heat flow imbalance was recorded as a blank array for a period of time sufficient for temperature equilibrium to be achieved. (5) Each ampoule was removed and dismantled. (6) A known weight of calibrant was placed in the sample-side glass tube and the ampoules were reassembled. (It is important to ensure that the same glass tube/ampoule combination is maintained throughout the analysis.) (7) The BAM operating temperature was raised by 1 °C. (8) Steps (3) and (4) were repeated and a known heat flow imbalance array was recorded. (9) The sample-side ampoule was removed and the calibrant was replaced with a known weight of the material whose specific heat was required. (10) The BAM operating temperature was raised by 1 °C. (11) Steps (3) and (4) were repeated and an unknown heat flow imbalance array was recorded. (12) The corrected peak areas were found by subtraction of the blank array from the known and unknown

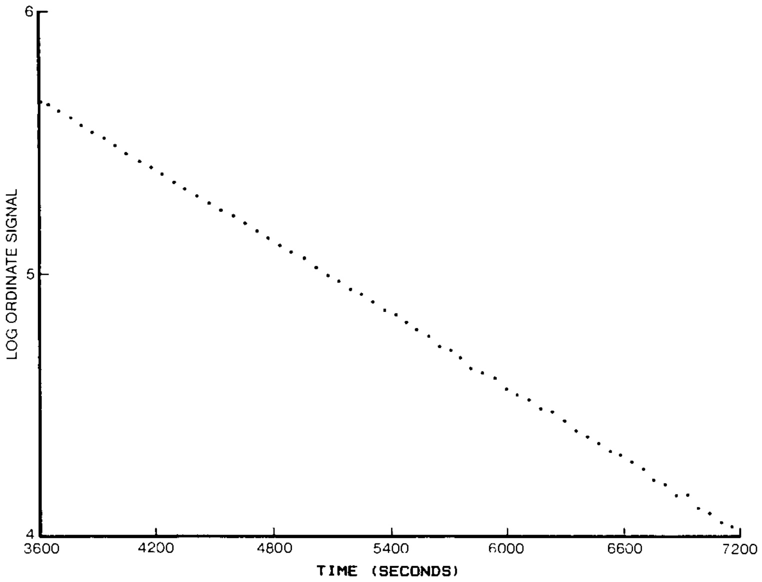

Fig. 4. Plot of log ordinate signal versus time—data taken from second hour of curve 3 in Fig. 1.

arrays. (13) The specific heat of the unknown sample was deduced by applying the algorithms described in the General Principles section. (14) Steps (9), (10), (11) and (12) were repeated for further unknown samples.

When mercury samples were analysed for technique assessment, a different sample was used with the original sample being removed from the BAM. The complete analysis procedure was followed in each case, so that changes

TABLE 1

Analysis of mercury samples

Sample number	Weight (mg)	Specific heat (J g^{-1} K^{-1})
1	8.540	0.135
2	11.163	0.135
3	15.084	0.134
4	18.823	0.136
5	16.530	0.135
6	16.025	0.136
7	14.452	0.134
8	15.224	0.136
9	6.808	0.134
10	8.226	0.135

Mean specific heat, 0.1349 J g^{-1} K^{-1}. Sample standard deviation, 0.000876 J g^{-1} K^{-1}. Conditions: samples held in stainless steel ampoules in glass liners; temperature dropped from 77 to 76 ° C.

TABLE 2

Analysis of some reactive materials

Sample	Specific heat (J g^{-1} K^{-1})
Water	4.217
Liquid gun propellant	2.279
Hydroxyl ammonium nitrate	2.260
Ottofuel II	1.767
Iso-propyl nitrate	1.910
Double base solid propellant	1.563
Triple base solid propellant	1.482
Triethanol ammonium nitrate	[a]

[a] See Discussion section (Range of application). Conditions: samples held in stainless steel ampoules in glass liners; temperature dropped from 77 to 76 ° C.

due to alteration in orientation of the ampoules, tightness of the screw cap, etc. could not be ignored.

A plot of ln ordinate signal versus time for the period 1–2 h after the temperature was dropped gave a straight line in all cases. An example of this can be seen in Fig. 4 which was plotted from the data collected during the second hour of the decay of a calibration standard. The analytical integration from 1 h to infinity suggested earlier therefore seems appropriate, and was used to find peak areas in all cases.

Evaluation

After calibration with alumina, the specific heats of 10 mercury samples were measured to evaluate the accuracy and precision of this technique. The results are summarised in Table 1.

Specific heat determination of unknown materials

The specific heats of a variety of substances of interest to the defence industry were measured in a similar manner, in order to find the range of applicability of the technique. The results are summarised in Table 2.

DISCUSSION

Assessment

The mean value for the specific heat of mercury was 0.1349 J g^{-1} K^{-1} with a standard deviation of 0.000876 J g^{-1} K^{-1}. This compares with a value of 0.1375 J g^{-1} K^{-1} reported by Douglas et al. [7].

The value found for water was 4.217 J g^{-1} K^{-1} compared with the value in the literature of 4.194 J g^{-1} K^{-1} [8].

Range of application

The specific heats of many of the substances listed in Table 2 are difficult to measure because of their reactive nature which causes heat generation both by exothermic decomposition and by incompatibility reactions with the walls of most types of calorimeter. In addition, some of them are volatile or dissolve in water with an associated release or consumption of energy. This makes it impractical to use traditional methods of specific heat determination, such as the method of mixtures.

In most cases, the method described here gives a reasonable value. This is because of the following: (a) the system is sealed; (b) the sample is contained in glass, which is chemically inert in most cases, and (c) although most of these samples will be generating some heat due to thermal decomposition, this will be effectively constant over a small temperature change. Since it is the area under the imbalance peak that is measured and not the total heat generation, the result will be unaltered by a steady, underlying, constant heat generation.

When an attempt was made to measure the specific heat of a sample of triethanol ammonium nitrate, this method gave a ludicrously high result—several times that of water. The reason for this became obvious when DSC was performed on the sample through this temperature region. The trace is shown in Fig. 5 and it can be seen that a sharp endotherm

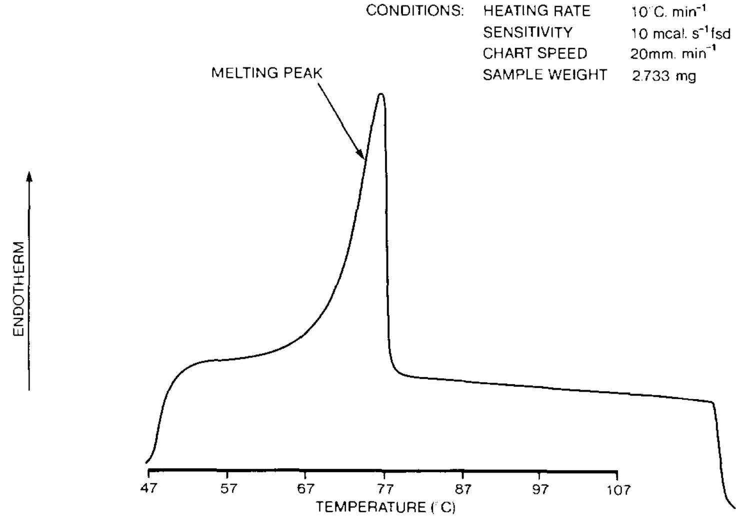

Fig. 5. DSC curve of triethanol ammonium nitrate.

occurs at 77 °C (due to the sample melting). Obviously this method is of no use under such circumstances.

No correction was made to allow for the difference in density of the various samples used in these measurements. Accuracy and precision would probably be improved if an allowance was made for the different amounts of air present in the calibration and sample ampoules.

CONCLUSIONS

The technique described here, which uses unmodified, commercially available equipment, appears capable of giving information of sufficient accuracy for use in the prediction of self-heating hazards of energetic materials. It can accommodate corrosive, exothermic and volatile behaviour, which are characteristics of materials likely to self-heat and which would make specific heat measurement by many other methods difficult.

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